

⑤

Int. Cl. 2:

A 01 N 9/22

⑱ **FEDERAL REPUBLIC OF GERMANY**

GERMAN



PATENT OFFICE

DE 28 28 222 A 1

⑪

Patent Application Pub. 28 28 222

⑫

Reference #:

P 28 28 222.6

⑬

Application Date:

06.28.1978

⑭

Publication Date:

01.10.1980

⑳

Priority:

⑳ ㉑ ㉒

—

㉔

Name:

Antidote for the protection of crops from herbicide damage

㉕

Applicant:

Bayer AG, 5090 Leverkusen

㉖

Inventor:

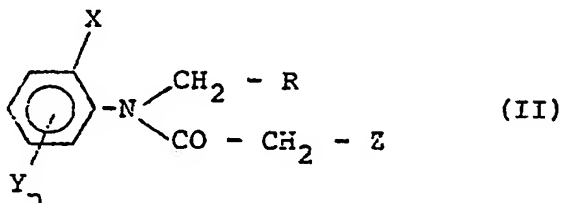
Riebel, Hans-Jochem, Dr.; Thomas, Rudolf, Dr.; 5600 Wuppertal;
Eue, Ludwig, Dr., 5090 Leverkusen; Faust, Wilfried, Dipl.-Landw. Dr.,
5068 Odenthal; Schmidt, Robert Rudolf, Dr., 5000 Köln

DE 28 28 222 A 1

Best Available Copy

Patent Claims

1. Agent for the protection of crops from damage due to herbicidal effective acetanilides with the chemical structure of



5 in which

R represents a potentially substituted, N-containing heterocyclic radical,

X and Y are the same or different, and represent alkyl,

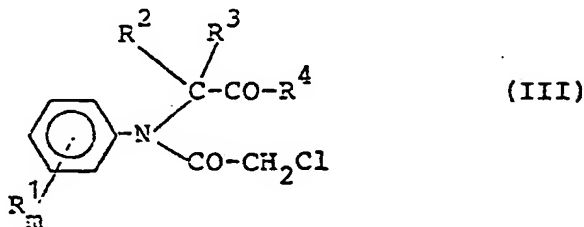
10 Z represents halogen, and

n represents 0, 1 or 2,

as well as their herbicidal acid additive salts and metal salt complexes,

- and or the chemical structure

15

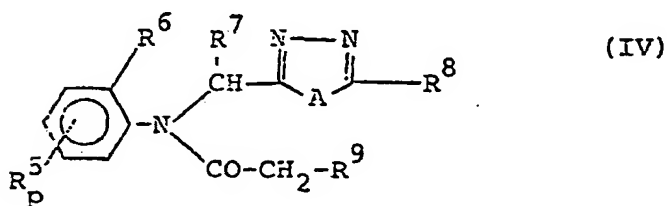


909882/0346

in which

- R represents alkyl, halogen, halogenalkyl, alacyl-thio, alacylsulfonyl, aminosulfonyl, cyano or nitro,
- 5 R^2 and R^3 are the same or different, and represent hydrogen, alacyl, halogen, halogenalkyl or potentially substituted phenyl,
- R represents alacyl or potentially substituted phenyl, and
- 10 m represents whole number from 0 to 5,

- or the chemical structure



in which

- 15 A represents oxygen, sulfur or the group $>NR^{10}$,
- R^7 represents hydrogen or alacyl,
- R^8 represents hydrogen, alacyl, halogenalkyl, alkenyl,

909882/0346

alkinyl, cycloalkyl, halogen, potentially substituted aryl and aralkyl or the groups $-OR^{11}$, $-SR^{11}$ and $NR^{10}R^{11}$.

5 R^{10} represents hydrogen, alanyl, or potentially substituted aryl,

R^{11} represents hydrogen, alanyl, halogenalkyl, alkenyl, alkinyl, cycloalkyl or potentially substituted aralkyl,

R^5 represents alanyl.

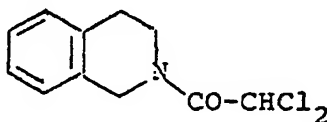
10 R^6 represents alanyl or halogen,

R^9 represents halogen, and

p represents the numbers 0, 1 or 2,

characterized by a content of N-dichloroacetyl-1,2,3,4-tetrahydro-isochinoline of the formula

15



2. Method for the protection of crops from damages caused by herbicidal acetanilides with the chemical structures (II), (III) and (IV) or by acid additive salts or metal salt complexes of agents with formula (II) per claim 1,

20

909882/0346

wherein N-dichloroacetyl-1,2,3,4-tetra-hydro-
isochinoline of formula (I) according to claim (I) is
allowed to act upon the crops and/or their habitat.

- 5 3. The use of N-dichloroacetyl-1,2,3,4-tetrahydro-isochinoline of
formula (I) according to claim 1 for the protection of
crops from damages caused by herbicidal acetanilides of
formulas (II), (III), and (IV) according to claim 1 and/or
10 due to acid additive salts or metal salt complexes of
formula (II) agents according to claim 1.
- 15 4. Method for the preparation of agents for the protection
of crops from damages caused by herbicidal acetanilides
of formulas (II), (III), and (IV) according to claim 1
and/or acid additive salts or metal salt complexes of
formula (II) agents according to claim 1, wherein
N-dichlorine-acetyl-1,2,3,4-tetrahydro-isochinoline of
formula (I) according to claim 1 is mixed with dilutants
and/or surface-active agents.
- 20 5. Agent for the selective weed control in economic crops,
characterized by a content of an agent combination
consisting of K-dichloroacetyl-1,2,3,4-tetrahydro-
isochinoline of formula (I) according to claim 1 and at
least one acetanilide of formula (II), (II) or (IV)
according to claim 1 and/or an acid additive salt or
metal salt complex of an agent of formula (II) according
25 to claim 1.

909882/0346

- 5 -
~~- 58 -~~

2828222

6. The use of a combination of agents according to claim
5 for selective weed control in economic crops.

Le A 18 887

909882/0346

BAYER AKTIENGESELLSCHAFT 5090 Leverkusen, Bayerwerk
Central Office for Dü/AB/Kü
Patents, Trademarks & Licenses II b

Antidote for the protection of crops from damages
caused by herbicides

This invention pertains to the use of the known
N-dichloroacetyl-1,2,3,4-tetrahydro-isochinoline as
antidote for the protection of crops caused by certain
herbicidal acetanilides.

5 The invention further pertains to new combinations of
agents consisting of the known N-dichloroacetyl-1,2,3,4-
tetrahydroisochinoline and specific acetanilides, and which
exhibit specifically good selective herbicidal properties.

10 In this context, the terms "antidote" or "safener" describe
substances that are capable of antagonizing specifically
the damaging effects of herbicides on crops, i.e. of
protecting the crops without noticeably affecting the
impact of the herbicides on the weeds.

15

909882/0346

Le A 18 387

- 2 -
- 7 -

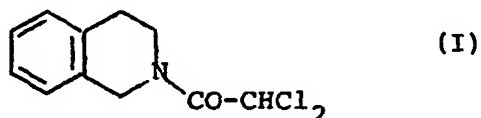
2828222

5 It is known that certain acetanilides being used to kill weeds in corn and other crops are causing more or less severe damages to the crops. It is further known that compounds like N-dichloroacetyl-2-methyl-indoline and N-dichloroacetyl-cis, trans-decahydrochinoline are suitable to reduce acetanilide damage to the crops (see also DE-OS 2 218 097). However, the effectiveness of these substances as antidote is not always completely satisfactory.

10

15 In addition, N-dichloroacetyl-1.2.3.4-tetrahydro-isochinoline has already been described as a substance with pharmacological properties (see also J. Med. Chem. 9 (5), 704-707 (1966)). It is furthermore known that the seeds of economic crops can be protected from herbicides prior to rooting by treating the seeds prior to sowing with N-dichloroacetyl-1,2,3,4-tetrahydro-isochinoline (see also DE-OS 2 245 471).

20 It has now been determined that the known N-dichloroacetyl-1.2.3.4-tetrahydro-isochinoline of formula



is exceptionally well suited to protect crops from damages caused by herbicidal acetanilides.

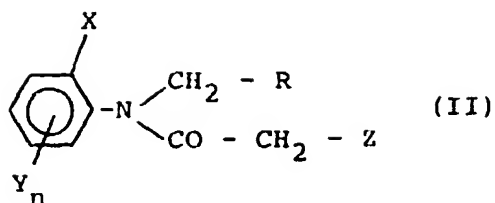
25 - of formula

909882/0346

Le A 18 887

- 8 -
- 3 -

2828222



in which

R stands for a potentially substituted
N-containing heterocyclic radical,

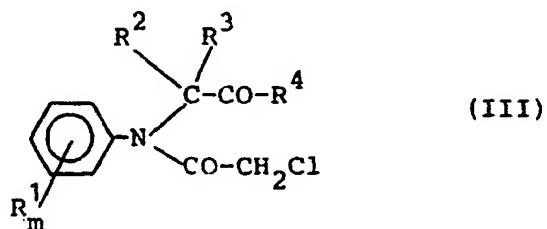
5 X and Y are the same or different, and stand
for alcy1,

Z stands for halogen, and

n stands for 0, 1 or 2,

10 as well as their herbicidal acid additive salts
and metal salt complexes,

- and of formula



in which

909882/0346

Le. A 18 887

- 9 -

2828222

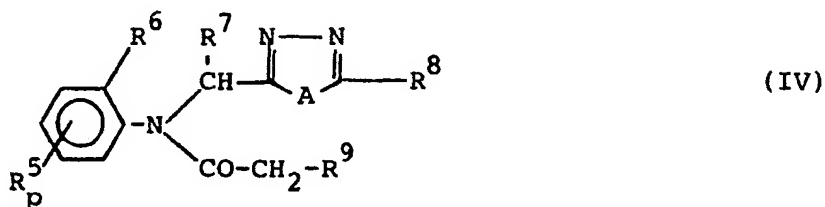
- 4 -

R stands for alacyl, halogen, halogenalkyl, alacylthio, alacylsulfonyl, aminosulfonyl, cyano or nitro,

5 R² and R³ are the same or different, and stand for hydrogen, alacyl, halogen, halogenalkyl or potentially substituted phenyl,

R⁴ stands for alacyl or potentially substituted phenyl, and

10 m stands for whole numbers from 0 to 5,
or of formula



in which

A stands for oxygen, sulfur or the group
>NR¹⁰,

15 R⁷ stands for hydrogen or alacyl,

R⁸ stands for hydrogen, alkyl, halogenalkyl, alkenyl,

909882/0346

Le A 18 887

alkinyl, cycloalkyl, halogen, potentially substituted aryl and aralkyl or the groups $-OR^{11}$, $-SR^{11}$ and $NR^{10}R^{11}$,

5 R^{10} stands for hydrogen, alcyl, or potentially substituted aryl,

R^{11} stands for hydrogen, alcyl, halogenalkyl, alkenyl, alkinyl, cycloalkyl or potentially substituted aralkyl,

R^5 stands for alcyl,

10 R^6 stands for alcyl or halogen,

R^9 stands for halogen, and

p stands for the numbers 0, 1 or 2,

to protect.

15 It was furthermore discovered that the new agent combinations consisting of N-dichloroacetyl-1,2,3,4-tetra-hydro-isochinoline of formula (I) and at least one acetanilide of formula (II), (III) or (IV) and an acid additive salt or metal salt complex of an agent of
20 of formula (II) are exceptionally well suited for the selective weed control in economic crops.

Surprisingly, herbicidal damages due to acetanilides of formulas (II), (III) and (IV) or due to acid additive salts or metal salt complexes of formula (II) agents to

909882/0346

crop plants with the simultaneous use of N-dichloroacetyl-
1,2,3,4-tetrahydro-isochinoline provides better suppression
than the use of the known compounds N-dichloro-acetyl-2-
methyl-indoline or N-dichloro-acetyl-cis, trans-deca-
5 hydrochinoline, being the chemically most similar
substances of the same agency. Based on the state of the
art it was also not to be expected that specifically the
N-dichloroacetyl-1,2,3,4-tetrahydro-isochinoline could
also serve as an antidote for the protection of crops from
10 damages due to herbicidal acetanilides of formulas (II),
(III) and (IV) or due to the acid additive salts or metal
salt complexes of agents of formula (II) when not applied
to the seeds but through surface application. - It is also
surprising that the agent combinations according to the
15 invention exhibit better selective herbicidal properties
than agent combinations consisting of at least one
acetanilide of formula (II), (III) or (IV) and N-
dichloroacetyl-2-methyl-indoline, a known antidote or the
other, also known antidote, N-dichloroacetyl-cis,trans-
20 decahydrochinoline.

The N-dichloroacetyl-1,2,3,4-tetrahydro-isochinoline of
formula (I) to be used according to the invention is
already known (see also J. Med. Chem. 9 (5), 704-707
(1966)). It can be produced by converting 1,2,3,4-
25 tetrahydro-isochinoline with dichloro-acetylchloride
potentially in the presence of an acid binder like
triethylamine, dimethylbenzylamine or pyridine, and
potentially in the presence of a diluting agent

30

909882/0346

Le A 18 887

5 like acetonitrile, at temperatures between 0 °C and 60 °C, preferably between 20 °C and 50 °C. - In this conversion, excess 1.2.3.4-tetrahydro-isochinoline can also function simultaneously as acid binding agent. In this case, no additional acid binder is required.

10 The 1,2,3,4-tetra-hydro-isochinoline required as the starting product can be obtained through hydration of isochinoline with gaseous hydrogen in the presence of a catalyst like Raney-nickel or ruthenium on a carrier substance, and potentially in the presence of a dilutant like methanol or ethanol, at temperatures between 100 °C and 250 °C, preferably between 150 °C and 200 °C. The hydrogen pressure can be varied across a larger range. Generally, the working pressure values are between 100 and 200 bar, preferably between 150 and 190 bar. Preferred is the hydration of isochinoline in the absence of additional dilutants, and with the use of ruthenium on aluminum oxide as catalyst.

20 The practical production according to the invention of the N-dichloroacetyl-1.2.3.4-tetrahydro-isochinoline of formula (I) is described in the following embodiments:

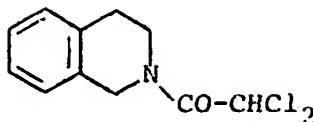
25

909882/0346

1. A 10 327

Embodiment 1

(I)



A solution of 29 g (0.22 mol) of 1,2,3,4-tetrahydro-
isochinoline in 200 ml acetonitrile is converted at room
5 temperature under agitation with 14.8 g (0.1 mol) of
dichloroacetylchloride. Afterwards, the mixture is
agitated for 2 additional hours at 40 °C. After being
cooled, the reaction mixture is added to water. The
resulting mixture is extracted multiple time with
10 methylene chloride. The wedded organic phases are
consecutively washed with diluted hydrochloric acid
and water, dried via Na₂SO₄, and concentrated under
reduced pressure. The remaining residue is
recrystallized from ligroin. The result is 16 g of N-
15 di-chloroacetyl-1,2,3,4-tetra-hydro-isochinoline from
the melting point at 88 °C.

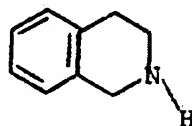
Analysis: C₁₁H₁₁Cl₂NO

Calculated: 54, 12 % C; 4.54 % H; 29.05 % Cl; 5.73 % N

Actual: 54.3 % C; 4.6 % H; 28.8 % Cl; 5.6 % N

20 Embodiment 2

(V)



129 g (1 mol) isochinoline are mixed with 15 g of a catalyst mixture consisting of ruthenium on aluminum oxide, and are hydrated for 2 hours at 190 °C under a hydrogen pressure of 170 to 190 bar. The reaction mixture is then filtered and subjected to a fractionated distillation. The result is 115 g of 1, 2, 3, 4-tetrahydroisochinoline.

Boiling point: 115 °C at 24 mm Hg.

90908. 0346

A. 11. 002

N-dichloroacetyl-1,2,3,4-tetrahydro-isochinoline **2828222**

of formula (I) to be used according to the invention

is suitable - as already mentioned - to protect
economic crops from damages caused by herbicidal

5 acetanilides of formulas (II), (III) and (IV).

Exact samples of acetanilides of formula (II) are:

2-methyl-6-ethyl-N-(pyrazole-1-yl-methyl)-chloroacetanilide

2,6-diethyl-N-(pyrazole-1-yl-methyl)-chloroacetanilide

10 2,6-diethyl-N-(1,2,4-triazole-1-yl-methyl)-chloroacetanilide

2,6-dimethyl-N-(1,2,4-triazole-1-yl-methyl)-chloroacetanilide

2-methyl-N-(pyrazole-1-yl-methyl)-chloroacetanilide

2,5-dimethyl-N-(pyrazole-1-yl-methyl)-chloroacetanilide

2,3-dimethyl-N-(pyrazole-1-yl-methyl)-chloroacetanilide

15 2-methyl-6-ethyl-N-(pyrazole-1-yl-methyl)-chloroacetanilide
hydrochloride

2,6-diethyl-N-(pyrazole-1-yl-methyl)-chloroacetanilide-
hydrochloride

20 2,6-Diethyl-N-[(3,5-dimethyl-pyrazole-1-yl)-methyl]-chloro-
acetanilide

2,6-diethyl-N-[13-chloro-1,2,4-triazolyle)-methyl]-chlorate-
tailed

2-methyl-6-ethyl-N-[(3,5-dimethyl-pyrazole-1-yl)-methyl]-
chloroacetanilide

25 2-tert.-butyl-N-(pyrazole-1-yl-methyl)-chloroacetanilide

2-methyl-6-ethyl-N-[(3-brom-5-methyl-pyrazole)-methyl]-
chloroacetanilide

2-methyl-6-ethyl-N-[(4-chloro-pyrazole-1-yl)--methyl]-chloro-
acetanilide

30 2-methyl-6-ethyl-N-[(3-chloro-1,2,4-triazolyle)-methyl]-
chloroacetanilide

909882/0346

Le A 18 887

Individual samples of acetanilides of formula (III) are:

2,6-dimethyl-N-(benzoyl-methyl)-chloroacetanilide
2,6-dimethyl-N-(4-chlorobenzoyl-methyl)-
5 chloroacetanilide

Individual samples for acetanilides of formula (IV) are:

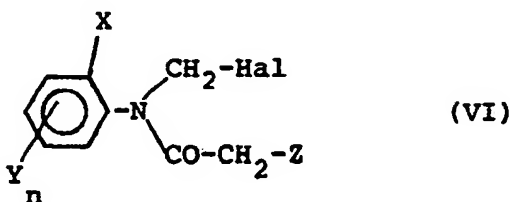
2,6-diethyl-N[2-methyl-1,3,4-oxadiazole-5-yl)-methyl]-
chloroacetanilide
2,6-dimethyl-N-[(2-methyl-1,3,4-oxadiazole-5-yl)-methyl]-
10 chloroacetanilide
2-ethyl-6-methyl-N-[(2-methyl-1,3,4-oxadiazole-5-yl) -
methyl]-chloroacetanilide
2-tert.-Butyl-N-[(2-methyl-1,3,4-oxadiazole-5-yl)-
methyl]-chloroacetanilide

15

The herbicidal acetanilides of formula (II) as well as their acid additive salts and metal salt complexes are not known yet. However, they can be produced by

a) N-halogenmethyl-halogenacetanilide of formula

20



909882/0346

in which

X, Y, Z and n have the above-indicated meaning

Hal stands for halogen, especially chlorine or bromine,

5 with hetero-cycles of formula



in which

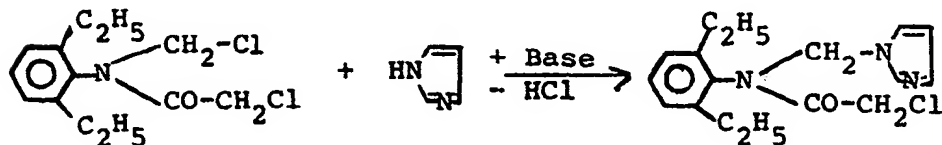
R has the above-indicated meaning, und

M stands for hydrogen or an alkali metal,

10 potentially in the presence of a dilutant and an acid binder converted, and potentially afterwards adding an acid or a metal salt.

If 2,6-diethyl-N-chloromethyl-chloroacetanilide and pyrazole are used as base materials, the reaction sequence of the method (a) can be described with the following chemical structure:

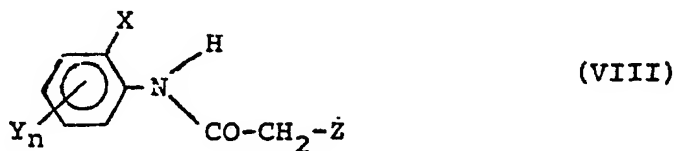
15



Die N-halogenmethyl-halogenacetanilides to be used in process (a) as base materials are generally defined by formula (VI). In this formula, X and Y are equal or different, and stand preferably for straight-chained or
5 branched alkyl with 1 to 4 carbon atoms. Z stands preferably for the halogens chlorine or bromine, and the index n has the above-indicated meaning.

The N-halogenmethyl-halogenacetanilides of formula (VI) are known or can be prepared according to known methods
10 (see also US Patent Specifications 3 630 716 and 3 637 847). They can be obtained, for example, by converting the according anilines with paraformaldehyde in the presence of catalytic amounts of potassium hydroxide, and mixing the resulting phenylazomethines with a halogenacetylhalogenide,
15 like chloroacetylchloride, for example.

The N-halogenmethyl-halogenacetanilides of formula (VI) can also be obtained with a new method by converting known halogenacetanilides of formula



20 in which

X/Y/Z and n have the above-indicated meaning,

with at least 1 mol formaldehyde or formaldehyde-emitting substances, e.g. paraformaldehyde, and a halogenation agent, like a halogen hydrogen acid or an inorganic or

909882/0346

organic acid halogenide as well as a water-binding agent, for example, sodium sulfate, in an inherently known way at temperatures between -10°C and 150°C , preferably between 10 and 70°C , potentially in the presence of an inert
5 organic solvent like toluene, for example (see also German Patent Publications 2 119 518 and 2 210 603). When inorganic acid halogenides are used, like thionylchloride, special water binders are not required (see also manufacturing embodiments).

10

The heterocycles also to be used as base materials are generally defined in formula (VII). In this formula, R stands preferably for the potentially substituted azoly-radicals
15 pyrazole-1-yl, imidazole-1-yl, 1,2,4-triazole-1-yl; 1,2,3-triazole-1-yl; 1,3,4-triazole-1-yl and 1,2,3,4-tetrazole-1-yl and for potentially substituted pyrrole-1-yl. Preferable substitutions to be considered are: halogen, in particular fluorine, chlorine, and bromine as well as
20 alkyl with 1 to 4 carbon atoms. M stands preferably for hydrogen, and the alkali metals sodium and potassium.

The heterocycles of formula (VII) are generally known compounds of organic chemistry.

Dilutants for the conversion in accordance to process (a)
25 to be considered are preferably inert organic solvents. They include preferably ketones like diethylketone, especially methylisobutylketone; nitriles like propionitrile, especially acetonitrile; ethers like tetrahydrofuran or dioxane; aliphatic and aromatic

30

909882/0346

Le A 18 887

hydrocarbons like petroleum ether, benzene, toluene or xylene, halogenated hydrocarbons like methylenechloride, tetrachlorohydrocarbon, chloroform or chlorobenzene; esters like ethyl acetate; and formamides, in particular
5 dimethylformamide.

Any normally used inorganic and organic acid acceptors can be used as acid binders for method (a). They include preferably alkaline carbonates, e.g. sodium carbonate, potassium carbonate and sodiumhydrogencarbonate, also
10 lower tertiary alkyamines, aralkylamine, aromatic amines or cycloalkylamines like triethylaniline, dimethylbenzylamine, pyridine and diazabicyclooctane. It is also possible to use a corresponding azole excess which, in this case, means a compound of formula (VII).

15 In method (a), the reaction temperatures can be varied across a larger range. The general range is about 0 to 120 °C, preferably between 20 and 80 °C.

In performing method (a), for 1 mol of the compounds of
20 formula (VI) preferably 1 to 2 mol of the heterocyclene of formula (VII) and 1 mol acid binder are used. To isolate the compounds of formula (II), the reaction mixture is filtered, the filtrate is washed with water, dried and concentrated. The residue can be cleaned potentially by fractionated crystallization or distillation.

25

909882/0346

Le A 18 887

- In a special form of processing, the reaction mixture is cooled to about 0°C, filtered and hydrogen chloride is introduced into the filtrate at 5 to -15 °C. The precipitating chloride salts are suctioned off, washed
- 5 with an organic solvent, e.g. ethyl acetate, and distributed in a mixture of an organic solvent, e.g. ethyl acetate and water with a pH-value of around 12. The organic phase is separated, and the compounds of formula (II) are isolated in the known manner.
- 10
- For the preparation of acid additive salts of the compounds of formula (II) all physiologically compatible acids can be used. They include preferably the halogen hydrogen acids, e.g. hydrochloric acid and hydrobromic acid, especially hydrochloric acid, also phosphoric acid,
- 15 nitric acid, sulfuric acid, mono- and bifunctional carbon acids and hydroxy carbon acid, fumaric acid, tartaric acid, citric acid, salicylic acid, sorbic acid, lactic acid, as well as sulfonic acids, e.g. p-toluene sulfonic acid, and 1,5-naphthalene disulfonic acid.
- 20
- The salts of the compounds of formula (II) can be obtained in a simple manner according to the usual salt creation methods, e.g. by solution of a formula (II) compound in a suitable, inert solvent, and the addition of the acid, e.g. hydrochloric acid, and can be isolated in the known
- 25 manner, and cleaned by washing with an inert organic solvent.

30

909882/0346

Le A 18 387

The preparation of metal salt complexes of compounds of formula (III), preferably uses salts of metals of the II. to IV. major and the I. and II. as well as the IV. to VIII. minor group, whereby copper, zinc, manganese,
5 magnesium, stannous, iron and nickel may be listed here as samples. As anions to be used are such that are derived from physiologically compatible acids. They include hydrohalogenic acids like hydrochloric acid and hydrobromic acid, as well as phosphoric acid, nitric acid,
10 and sulfuric acid.

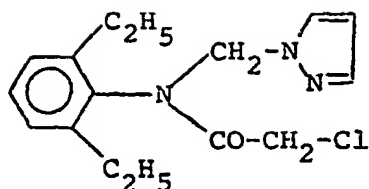
The metal salt complexes of the compounds of formula (II) can be obtained in a simple manner according to the usual procedures, e.g. by dissolving the metal salt in alcohol, e.g. ethanol, and adding it to the compound of formula
15 (II). The metal salts complexes can be cleaned in a known manner, e.g. through filtering, isolation and recrystallization, if necessary.

The practical preparation of acetanilides of formula (II) can be obtained from the following embodiments.
20

909882/0346

Le A 18 887

Embodiment 3



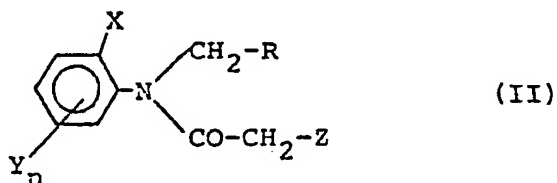
A mixture of 68 g (1 mol) pyrazole and 106 g (1.05 mol) triethylamine in 150 ml anhydrous ethyl acetate are added to 274.2 g (1 mol) 2,6-Diethyl-N-chloromethyl-chloroacet-anilide under agitation, whereby the temperature increases to 30°C. The mixture is then stirred for another hour at room temperature. The processing offers two options:

- 1) The reaction mixture is filtered, the filtrate is neutrally washed with water, dried via sodium sulfate, and evaporated in the vacuum. After a fractionated crystallization with ligroin, the result is 171.2 g (56% of theory) of 2,6-diethyl-N-(pyrazole-1-yl-methyl)-chloroacetanilide from melting point 67°C in the form of clear crystals.
- 2) The reaction mixture is cooled to 0°C, filtered and the filtrate is washed with 10 ml of cold ethyl acetate. 50 g (1.4 mol) of dry hydrogen chloride are introduced into the filtrate at 0 to -10°C. Afterwards, the precipitated salts are suctioned off, washed with 50 ml of cold ethyl acetate, and the solid residue is distributed between 0.5 l ethyl acetate and

909882/0346

- a 0.5 l watery sodium hydroxide solution with a pH-value of 12. The organic phase is separated, washed twice with 0.5 l sodium chloride solution, dried via sodium sulfate, and evaporated in the vacuum. The
- 5 colorless, oily residue is mixed with 60 ml benzene, where it crystallizes. The result is 220.2 g (72% of theoretical value) of 2,6-diethyl-N-(pyrazole-1-yl-methyl)-chloroacetanilide from a melting point of 67°C in the form of colorless crystals.
- 10 The compounds listed in the following table are made in an analogous manner:

Table 1



Sample No.	X	Y _n	Z	R	Melting point
4	C ₂ H ₅	6-C ₂ H ₅	Cl	1,2,4-Triazole-1-yl	112
5	i-C ₃ H ₇	6-i-C ₃ H ₇	Cl	Pyrazole-1-yl	134
6	CH ₃	6-C ₂ H ₅	Cl	1,2,4-Triazole-1-yl	92
7	CH ₃	6-C ₂ H ₅	Cl	Pyrazole-1-yl	57
8	C ₂ H ₅	4,6-(CH ₃) ₂	Cl	Pyrazole-1-yl	32
9	CH ₃	4,6-(CH ₃) ₂	Cl	Pyrazole-1-yl	92
10	C ₂ H ₅	4-CH ₃ , 6-C ₂ H ₅	Cl	Pyrazole-1-yl	78
11	i-C ₃ H ₇	6-i-C ₃ H ₇	Cl	1,3,4-Triazole-1-yl	196
12	i-C ₃ H ₇	6-i-C ₃ H ₇	Cl	1,2,4-Triazole-1-yl	138

909882/0346

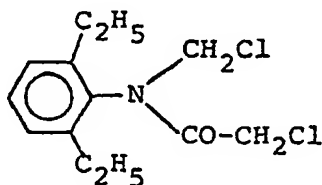
Table 1 (continued)

Sample No.	X	Yn	Z	R	Melting point (°C)
13	C ₂ H ₅	6-C ₂ H ₅	C1	Pyrrole-1-yl	Oel
14	i-C ₃ H ₇	-	C1	1,2,4-Triazole-1-yl	113
15	CH ₃	6-C ₂ H ₅	C1	1,2,3,4-tetrazoi-1-yl	Cel
16	i-C ₃ H ₇	-	C1	Pyrazole-1-yl	Cel
17	C ₂ H ₅	-	C1	1,2,4-Triazole-1-yl	81
18	CH ₃	6-CH ₃	C1	Pyrazole-1-yl	82
19	CH ₃	6-CH ₃	C1	1,2,4-Triazole-1-yl	110
20	CH ₃	5-CH ₃	C1	1,2,4-Triazole-1-yl	Oel
21	CH ₃	-	C1	Pyrazole-1-yl	55
22	CH ₃	-	C1	1,2,4-Triazole-1-yl	58
23	CH ₃	5-CH ₃	C1	Pyrazole-1-yl	Oel
24	CH ₃	3-CH ₃	C1	1,2,4-Triazole-1-yl	114
25	CH ₃	3-CH ₃	C1	Pyrazole-1-yl	102
26	C ₂ H ₅	6-CH ₃	C1	Pyrazole-1-yl (xHCl)	87
27	C ₂ H ₅	6-C ₂ H ₅	C1	Pyrazole-1-yl (xHCl)	67
28	C ₂ H ₅	6-C ₂ H ₅	C1	3,5-dimethyl-pyrazole-1-yl	111
29	C ₂ H ₅	6-C ₂ H ₅	C1	Bromo-methyl-pyrazolyl	145
30	C ₂ H ₅	6-C ₂ H ₅	C1	3-Chlor-1,2,4-triazole-1-yl	110
31	CH ₃	6-C ₂ H ₅	C1	3,5-dimethyl-pyrazole-1-yl	90
32	C ₂ H ₅	6-C ₂ H ₅	C1	3-methyl-pyrazole-1-yl	S9
33	C ₂ H ₅	6-CH ₃	C1	3-methyl-pyrazole-1-yl	113
34	C(CH ₃) ₃	-	C1	Pyrazole-1-yl	Oel
35	C(CH ₃) ₃	-	C1	1,2,4-Triazole-1-yl	118
36	C ₂ H ₅	6-CH ₃	C1	Bromo-methyl-pyrazolyl	80

909882/0346

Table 1 (continued)

Embod. #	X	Yn	Z	R	Melting point (°C)
37	CH ₃	6-C ₂ H ₅	Cl	4-Chlor- pyrazole-1-yl	91
38	CH ₃	6-C ₂ H ₅	Cl	3-Chlor-1,2,4- triazole-1-yl	121
39	C ₂ H ₅	6-CH ₃	Cl	2,4,5-Trichlor- imidazole-1-yl	158
40	C ₂ H ₅	6-C ₂ H ₅	Cl	4-Chlor- pyrazole-1-yl	110
41	C ₂ H ₅	6-C ₂ H ₅	Cl	1,2,3,4-tetra- zole-1-yl	110
42	C ₂ H ₅	6-C ₂ H ₅	Br	Pyrazole-1-yl	68
43	CH ₃	6-C ₂ H ₅	Br	Pyrazole-1-yl	67
44	C ₂ H ₅	6-C ₂ H ₅	Cl	Imidazole-1-yl	0el
45	C ₂ H ₅	6-C ₂ H ₅	Br	1,2,4-Triazole- 1-yl	90
46	CH ₃	6-C ₂ H ₅	Br	1,2,4-Triazole- 1-yl	78

Preparation of Starting ProductsEmbodiment 3 a

(Variation α)

- 5 Added to a solution of 225.7 g (1 mol) 2,6-Diethyl-chloroacetanilide in 1.5 l toluene are 45 g (1.5 mol) para-formaldehyde. Heat to 40 °C, and add 179 g (1.6 mol) of thiophyl chloride drops resulting in a lively development of gas, and agitate at 40°C until no more gas is produced.
- 10 This is followed by filtration, and the filtrate is concentrated in the vacuum.
- After degassing of the residue in high vacuum, the result is 268.7 g (98 % of theory) of 2,6-diethyl-N-chloromethyl-chloroacetanilide as a colorless oil.

15 (Variation β)

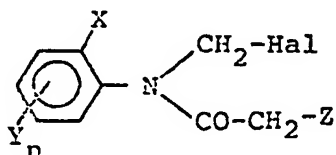
- Added to a solution of 225.7 g (1 mol) 2,6-diethyl-chloroacetanilide in 1,5 l anhydrous toluene are 45 g (1.5 mol) paraformaldehyde and 100 g anhydrous sodium sulfate. While agitating and heating to 50 °C, dry
- 20 hydrogen chloride is introduced until the milky suspension of the paraformaldehyde has disappeared. Afterwards, another 100 g of anhydrous sodium sulfate are added, followed by one hour of agitation at 50°C, and subsequent filtration. The filtrate is vacuum-concentrated.

909882/0346

After degassing the residue, the result is 263.2 (96 % of theoretical value) of 2,6-diethyl-chloroacetanilide as a colorless oil.

Analogous to Embodiment 3a, the compounds in the following Table 2 are the result.

5 Table 2



Embod. Number	X	Yn	Z	Hal	Melt. Point and Refractive Index
5 a	i-C ₃ H ₇	6-i-C ₃ H ₇	Cl	Cl	not isolated
6 a	CH ₃	6-C ₂ H ₅	Cl	Cl	91
8 a	C ₂ H ₅	4,6-(CH ₃) ₂	Cl	Cl	not isolated
9 a	CH ₃	4,6-(CH ₃) ₂	Cl	Cl	"
10 a	C ₂ H ₅	4-CH ₃ 6-C ₂ H ₅	Cl	Cl	"
14 a	i-C ₃ H ₇	-	Cl	Cl	90
17 a	C ₂ H ₅	-	Cl	Cl	not isolated
18 a	CH ₃	6-CH ₃	Cl	Cl	88
20 a	CH ₃	5-CH ₃	Cl	Cl	not isolated
24 a	CH ₃	3-CH ₃	Cl	Cl	40
34 a	C(CH ₃) ₃	-	Cl	Cl	not isolated
42 a	C ₂ H ₅	6-C ₂ H ₅	Br	Br	"
43 a	CH ₃	6-C ₂ H ₅	Br	Br	"

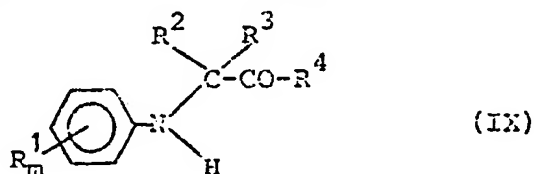
909882/0346

1975 18 687

The acetanilides of formula (II) exhibit strong herbicidal properties, especially against grasses. They can therefore be used as selective weed and especially weed grass killers.

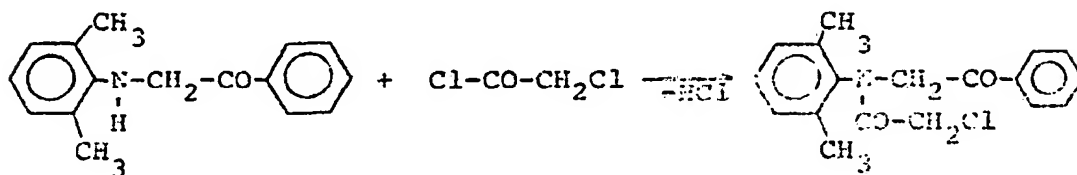
- 5 The herbicidal acetanilides of formula (III) are also not known yet. They can, however, be made by converting

b) N-Acylmethylanilines of formula



- 10 in which
 R^1, R^2, R^3, R^4 and m have the above-indicated meaning,
 chloroacetylchloride in the presence of a dilutant.

- If 2,6-dimethyl-N-benzoylmethyl-aniline and
 15 chloroacetylchloride as starting substances, the
 reaction sequence of the process (b) for the following
 formulas can be described:



909882/0346

The N-acylmethyl anilines to be used as base materials for process (b) are generally defined by formula (IX). In this formula, R^1 represents preferably straight-chained or branched alcyyl with 1 to 6, in particular 1 to 4 carbon
5 atoms, halogen, especially fluorine, chlorine, and bromine, halogenalkyl with up to 3 carbon and up to 5 equal or different halogen atoms, whereby especially fluorine and chlorine represent halogens (sample, trifluomethyl); furthermore, preferably for alkylthio and
10 alcyysulfonyl with 1 to 4 carbon atoms in the alcyyl part and for aminosulfonyl, cyano and nitro. R^2 and R^3 are equal or different, and stand preferably for hydrogen, straight-chain or branched alkyl with 1 to 4 carbon atoms, halogen, especially fluorine, chlorine, and bromine, halogen alkyl
15 with up to 3 carbon and up to 5 equal or different halogen atoms, whereby fluorine and chlorine stand especially for halogens as well as preferably for potentially simple or multiple substituted phenyl, where, preferably, substitutes for R^1 will be used. R^4 stands preferably for
20 straight-chain or branched alkyl with 1 to 6, especially 1 to 4 carbon atoms as well as for potentially simply or multiply substituted phenyl, whereby as substitutions preferably the already known moieties as well as phenyl and phenyloxy, which also may be substituted by R^1 , will be
25 used.

1

The N-acylmethyl-anilines of formula (IX) are known (see (Chem. Ber. 25, 2965 (1892) as well as Chem. Soc. 1943, 63) or can be produced with the use of known

30 .

909882/0346

Le A 18 2:7

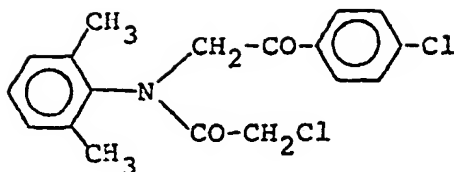
methods. They result, for example, when anilines are converted with α -halogen ketones in the presence of organic solvents like ethanol (see also manufacturing embodiments).

- 5 Dilutants for the conversion according to method (b) are preferably inert organic solvents. They include preferably ketones like diethylketone, especially acetone and methylethylketone; nitriles like propionitrile, especially acetonitrile; ether like
- 10 tetrahydrofuran or dioxane; aliphatic and aromatic hydrocarbons like petroleum ether, benzene, toluene or xylol;
halogenated hydrocarbons like methylenechloride, tetrachlorocarbon, chloroform or chlorobenzene;
- 15 The reaction temperatures during process (b) can be varied over a greater range. In general, the working temperatures are between 0 and 120 °C, preferably between 20 and 100 °C.

Process (b) uses preferably for 1 mol of the compound of
20 formula (IX) 1 to 3 mol of chloroacetylchloride. The isolation of the compounds of formula (III) takes place in the known manner.

The practical preparation of acetanilides of formula (III) is illustrated on the following embodiments:

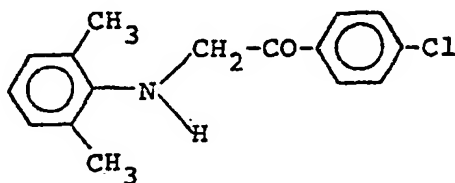
909882/0346

Embodiment 47

Added to a solution of 18.5 g (0.068 mol) of 2,6-dimethyl-N-(4-chlorobenzoylmethyl)-aniline in 150 ml benzene are
 5 16 ml (0.2 mol) chloroacetylchloride by pipette.
 Thereafter, the mixture is agitated under reflux and
 concentrated by vacuum distillation of the solvent and the
 excess chloroacetylchloride. The residue is levigated with
 a mixture of ether/petroleum ether (1:3), the resulting
 10 crystalline residue is suctioned off and dried. The result
 is 17.7 g (75% of theory) of 2,6-dimethyl-N-(4-chlorobenzoylmethyl)-chloroacetanilide with a melting
 point of 128°C.

Preparation of the base product

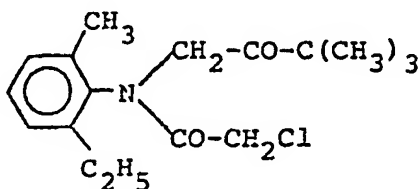
15



46.7 g (0.2 mol) ω-bromin-4-chloroacetophenon in 40 ml
 ethanol are added to 48.4 g (0.4 mol) 2,6-dimethylaniline

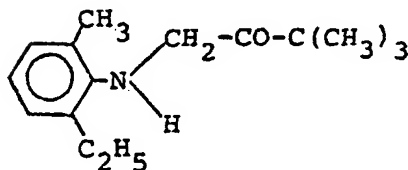
in 40 ml ethanol and heated for 20 minutes to 50°C, then cooled to 0°C, filtered the resulting crystals and washes them with a small amount of ethanol. The result is 30 g (55% of theoretical value) 2,6-dimethyl-N-(4-chloroben-

Embodiment 48



23.3 g (0.1 mol) 2-ethyl-6-methyl-N-pivaloylmethyl-aniline are dissolved in 100 ml benzene and mixed with 24 ml
10 (0.3 mol) of chloroacetylchloride. The mixture is then agitated for 15 hours under reflux, and concentrated by vacuum distillation of the solvent and excess chloroacetylchloride. The oily residue is mixed with petroleum ether, decanted, mixed with activated charcoal, filtered
15 and vacuum-concentrated. The residue is mixed with n-hexane, the resulting solid is suctioned off and dried. The final result is 13.7 g (45 % of theoretical value) 2-ethyl-6-methyl-N-pivaloylmethyl-chloroacetanilide with a melting point of 86°C.

20 Preparation of the base product



909882/0346

103 g (0.8 mol) 2-ethyl-6-methyl-aniline and 53.8 g
(0.4 mol) monochloropinakoline are heated in 300 ml
toluene for 25 hours to 110°C. The mixture is cooled,
filtered, the filtrate is washed with water, dried via
5 sodium sulfate, and concentrated via vacuum-distillation
of the solvent. The residue is fractionatedly distilled.
The result is 24.1 g (26 % of theoretical value) 2-
ethyl-6-methyl-N-pivaloylmethyl-aniline with a boiling
point of 138 to 150°C/0.7 mm and a refractive index of
10 $n_D^{20} = 1.5168$.

The compounds listed in the following table 3 are
prepared in an analogous manner.

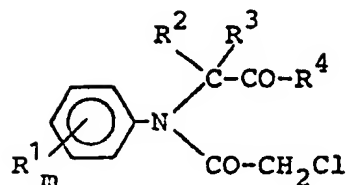
909882/0346

-35-

2828222

- 30 -





Table 3



Emb. No.	R ¹ _m	R ²	R ³	R ⁴	Melting Point °C & Refractive Index
49	2-CH ₃	H	H		138
50	2-CH ₃	H	H		140
51	2,6-(C ₂ H ₅) ₂	H	H		134
52	2,6-(C ₂ H ₅) ₂	H	H		116
53	2-Cl	H	H		124
54	2,6-(CH ₃) ₂	H	H		100
55	4-Cl	H	H		114
56	2,6-(CH ₃) ₂	CH ₃	H	CH ₃	104
57	2,6-(i-C ₃ H ₇) ₂	H	H		200
58	2,6-(C ₂ H ₅) ₂ , 4-CH ₃	H	H		112
59	2,6-(i-C ₃ H ₇) ₂	H	H		140
60	2,6-(CH ₃) ₂	H	H		90
61	2-C ₂ H ₅ , 6-CH ₃	H	H		70
62	2,6-(CH ₃) ₂	H	H		114
63	2-C ₂ H ₅ , 4,6-(CH ₃) ₂	H	H		n _D ²⁰ =1,5680
64	2,6-(CH ₃) ₂	H	H		104
65	2,4,6-(CH ₃) ₃	H	H		134

909882/0346

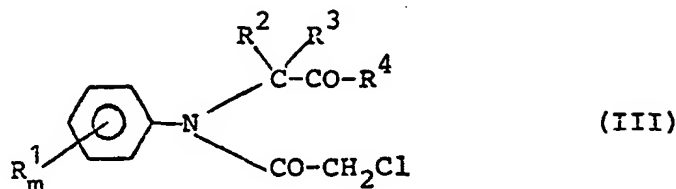
Table 3 (continued)

Emb. No.	R ¹ _m	R ²	R ³	R ⁴	Melting Point °C & Refractive Index
66	2,4,6-(CH ₃) ₃	H	H		n _D ²⁰ =1,5610
67	2,6-(CH ₃) ₂	H			149
68	2,6-(CH ₃) ₂	H	CH ₃		84

909882/0346

The compounds listed in the following table 4 can be obtained in an analogous manner.

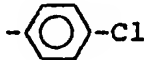
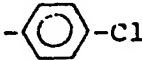
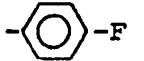
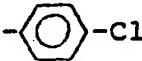
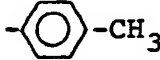





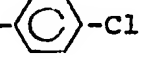
Table 4



Emb. No.	R _m ¹	R ²	R ³	R ⁴
69	3,5-(CF ₃) ₂	H	H	
70	2,6-(CH ₃) ₂	H	H	
71	2,6-(CH ₃) ₂	H	H	
72	2,6-(CH ₃) ₂	H	H	
73	2,6-(CH ₃) ₂ , 4-SO ₂ NH ₂	H	H	
74	2-Cl, 6-CH ₃	H	H	
75	2-C ₂ H ₅ , 6-CH ₃	CH ₃	CH ₃	
76	2-C ₂ H ₅ , 6-CH ₃	CH ₃	CH ₃	
77	2-C ₂ H ₅ , 6-CH ₃	CH ₃	CH ₃	
78	2-C ₂ H ₅ , 6-CH ₃	CH ₃	CH ₃	
79	2-C ₂ H ₅ , 6-CH ₃	CH ₃	CH ₃	
80	2-C ₂ H ₅ , 6-CH ₃	H	CH ₃	
81	2-C ₂ H ₅ , 6-CH ₃	H	CH ₃	

909882/0346

Table 4 (continued)

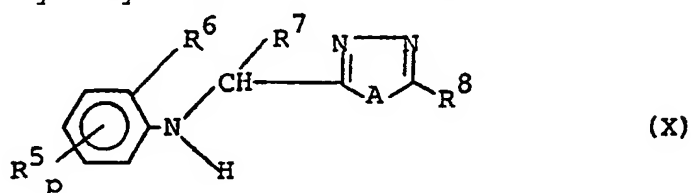
Emb. Nr.	R ¹ _m	R ²	R ³	R ⁴
82	2,6-(CH ₃) ₂	H		
83	2,6-(CH ₃) ₂	H		
84	2,6-(CH ₃) ₂	H		
85	2,6-(CH ₃) ₂	H		
86	2,6-(CH ₃) ₂	H		
87	2,6-(CH ₃) ₂	H	CH ₃	

909882/0346

The acetanilides of formula (III) exhibit strong herbicidal properties. They are therefore suitable for use in weed control. They may, in particular, be applied to selective weed and grass control.

- 5 The herbicidal acetanilides of formula (IV) are also not known at the present. However, they can be prepared by converting

c) N-azolyalkylanilines of formula

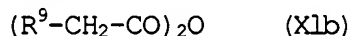


- 10 in which
R⁵, R⁶, R⁷, R⁸, A and p have the above-indicated meaning,

with halogen succinic acid chlorides or anhydrides of the chemical formulas

- 15 R⁹-CH₂-CO-Cl (XIa)

and/or



in which

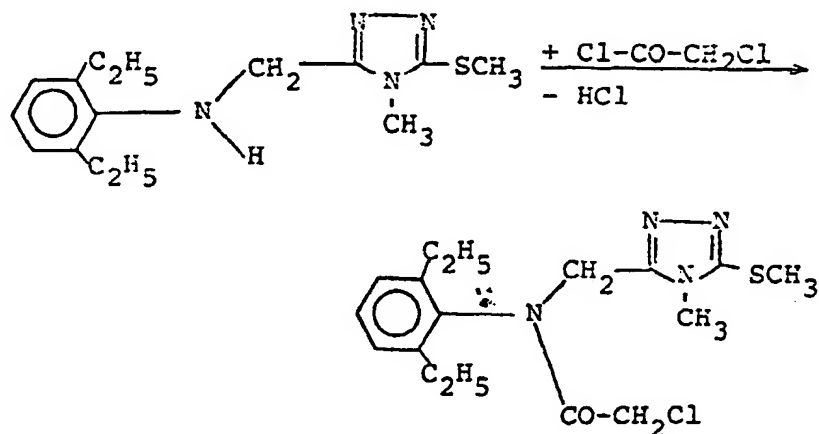
R⁹ has the above-indicated meaning,

- 20 in the presence of a dilutant and the presence of an acid-binding agent, if necessary.

909882/0346

If 2,6-diethyl-N-(3-methylthio-4-methyl-1,2,4-triazole-5-yl-methyl)-aniline and chloroacetylchloride are used as base materials, the reaction sequence of process (c) can be illustrated by the following formula:

5



The N-azolyalkylanilines required as base materials for process (c) are generally defined by formula (X). In this formula, A stands preferably for oxygen, sulfur or the group -NR¹⁰, wherein R stands preferably for hydrogen, straight-chained or branched alacyl with 1 to 4 carbon atoms, and for aryl with 6 to 10 carbon atoms, in particular phenyl, whereby each of these aryl-moieties may be substituted by halogen, alacyl with 1 to 4 carbon atoms

15

alkoxy with 1 or 2 carbon atoms, alcylothio with 1 or 2
carbon atoms, cyano, nitro and/or halogenalkyl with up to
2 carbon and up to 5 equal or different halogen atoms,
naming fluorine and chlorine in particular as samples of
5 halogens. R^7 stands preferably for hydrogen or methyl.
 R^8 stands in formula (X) preferably for hydrogen, straight
chained or branched alcylothio with 1 to 4 carbon atoms,
halogenalkyl with up to 3 carbon and up to 5 equal or
different halogen atoms, whereby halogens are especially
10 represented by fluorine and chlorine, for example,
trifluoromethyl, also preferably for alkenyl and alkynyl
with 2 to 4 carbon atoms, cycloalkyl with 5 to 7 carbon
atoms as well as for halogen, especially fluorine,
chlorine or bromine. R^8 also preferably stands for
15 aryl with 6 to 10 carbon atoms, especially phenyl, whereby
each of these aryl moieties may be substituted by halogen,
alcylothio with 1 to 3 carbon atoms, alkoxy with 1 or 2 carbon
atoms, alkylthio with 1 or 2 carbon atoms, cyano, nitro
and/or halogenalkyl with up to 2 carbon atoms and up to
20 5 equal or different halogen atoms, whereby the halogens
are represented especially by fluorine or chlorine, with
trifluoromethyl specifically being named as a sample for
halogenalkyl. R^8 also stands preferably for aralkyl with
5 to 10 carbon atoms in the aryl part, and 1 to 4 carbon
25 atoms the alcylothio part, especially for benzyl, whereby each
one of these aralkyl moieties in the aryl part may be
substituted by halogen, alcylothio with 1 to 4 carbon atoms,
alcylothio with 1 or 2 carbon atoms, alcylothio with 1 or
2 carbon atoms, cyano, nitro and/or halogenalkyl

30

909882/0346

- with up to 2 carbon atoms and up to 5 equal or different halogen atoms, whereby halogens are represented specifically by fluorine and chlorine, with trifluormethyl being named as a sample of halogenalkyl.
- 5 R⁸ stands in addition for the groups -OR¹¹, -SR¹¹, and NR¹⁰R¹¹, wherein R¹⁰ stands preferably for those moieties, which have already been named above as preferable for this radical, R¹⁴ stands in these groups for hydrogen, straight-chain or branched alcy l with 1 to 4 carbon
- 10 atoms, halogenalkyl with 3 carbon and up to 5 equal or different halogen atoms, whereby the halogens are especially represented by fluorine and chlorine, with trifluormethyl being named as a sample; further preferably for alkenyl and alkynyl with 2 to 4 carbon
- 15 atoms, cycloalkyl with 5 to 7 carbon atoms as well as for aralkyl with 6 to 10 carbon atoms in the aryl part and 1 to 4 carbon atoms in the alcy l part, especially for benzyl, whereby each of these aralkyl moieties in the aryl part may be substituted by halogen, alcy l with 1 to
- 20 4 carbon atoms, alkoxy with 1 or 2 carbon atoms, alcy lthio with 1 or 2 carbon atoms, cyano, nitro and/or halogenalkyl with up to 2 carbon atoms and up to 5 equal or different halogen atoms, whereby the halogens are especially represented by fluorine and
- 25 chlorine, with trifluormethyl being named as a sample.

In of formula (X), R⁵ preferably stands for straight-chain or branched alcy l with 1 to 4 carbon atoms.

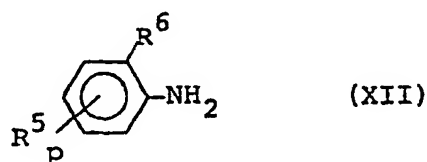
R⁶ stands in formula (X) preferably for straight-chain

909882/0346

or branched alcyyl with 1 to 4 carbon atoms or for the halogens fluorine, chlorine and bromine; the index p stands for the numbers 0, 1 or 2.

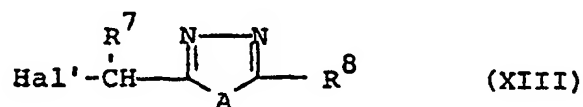
5 The N-azolyalkylanilines of formula (X) required in process (c) as base materials are not known yet. They are obtained when

d) Aniline of formula



10 in which
R⁵, R⁶ and p have the above-indicated meaning,

are converted with azole derivatives of formula



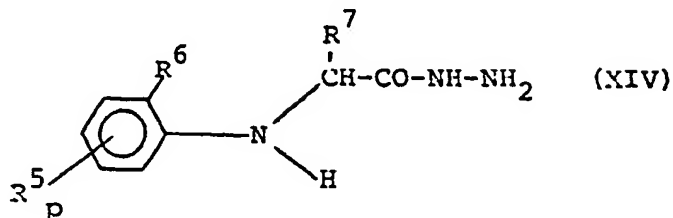
15 in which
A, R⁷ and R⁸ have the above-indicated meaning, und
Hal' stands for chlorine or bromine,

20 in the presence of acid binders, like potassium or sodium carbonate, and in the presence of inert organic solvents like dimethylformamide or toluene, at temperatures between 20 and 160°C, whereby preferably

909882/0346

excess of aniline of formula (XII) is being used
(see also preparation embodiments), or

e) hydrazine derivatives of formula



5

in which

R^5 , R^6 , R^7 and P have the above-indicated meaning

with isocyanates or mustard seed oil of formula



in which

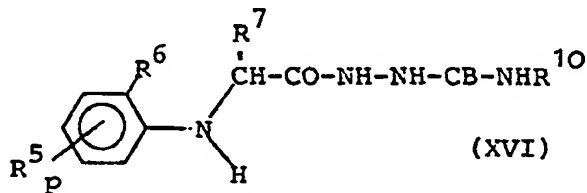
10

B stands for oxygen or sulfur, and

R^{10} has the above-indicated meaning,

in the presence of organic solvents, like alcohol
ether or hydrocarbons, at temperatures between 0 and
80°C, the resulting compounds of formula

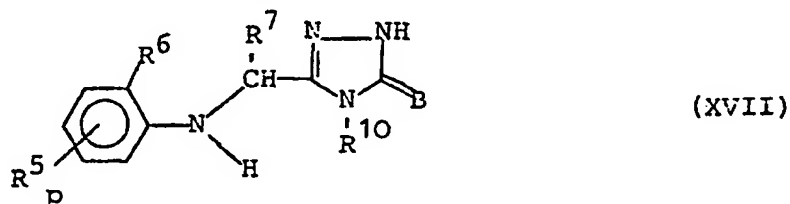
15



in which

B, R⁵, R⁶, R⁷, R¹⁰ and p have the above-indicated meaning

5 in the presence of a strong base, like sodium or potassium hydroxide solution, and in the presence of solvents like ethanol or water cycled at temperatures between 20 and 100°C and the resulting triazolones or triazolthiones of formula



10 in which B, R⁵, R⁶, R⁷, R¹⁰ and p have the above-indicated meaning, with halogenides of formula



15 in which Hal' stands for chlorine or bromine, and R¹² stands for the radicals of substitute R¹¹, with the exception of hydrogen,

20 converted in the presence of a strong base like sodium hydroxide, and in the presence of an inert organic solvent, like toluene or methylenechloride, at temperatures between 20 and 80°C, whereby phase transfer catalyzation and other alcyating agents, like dimethylsulfate, may be applied (see also preparation samples), or

25

909882/0346

f) hydrazine derivative of formula (XIV) converted with formic acid and acid chlorides or acid anhydrides of formula



or



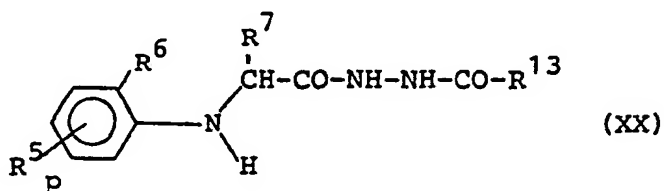
5

in which

R^{13} stands for alcylyl, halogenalkyl, alkenyl, alkynyl, cycloalkyl, potentially substituted aryl or potentially substituted Aralkyl

10 in the presence of an inert organic solvent, like an ether, hydrocarbon or halogen hydrocarbon at temperatures between 0 und 50°C, and where the resulting compounds with the formula

15



in which

R^5 , R^6 , R^7 , R^{13} and p have the above-indicated meaning,

20

are cyclicized either with diphosphorpentasulfide in a known manner, (see also Chem.Ber. _32f 797 (1899) and J. prakt. Chemie _69_, 145 (1904)) into thiadiazole derivatives or also in a known manner with common

using water-separating agents converts into
oxadiazole derivatives (see also Elderfield,
Heterocyclic Compounds, Vol. 7 (1961)) or

- 5 g) Hydrazine derivative of formula (XIV) with nitriles
of formula

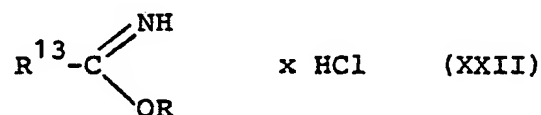


in which

R^{14} stands for a potentially substituted alcy1 or
potentially substituted aryl

- 10 converted in a known manner into triazole derivatives
(see also Chem.Ber. 96, 1064 (1963)), or

- h) hydrazine derivatives of formula (XIV) with
iminoethers with the formula



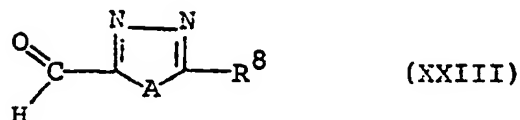
- 15 in which

R^{13} stands for alcy1, halogenalkyl, alkenyl, Alkiny1,
cycloalkyl, potentially substituted aryl or
potentially substituted aralkyl, and

R^{15} stands for methyl or ethyl,

- 20 is converted in a known manner under reflux and in the
presence of an inert organic solvent, like ethanol,
into oxadiazole derivatives, or

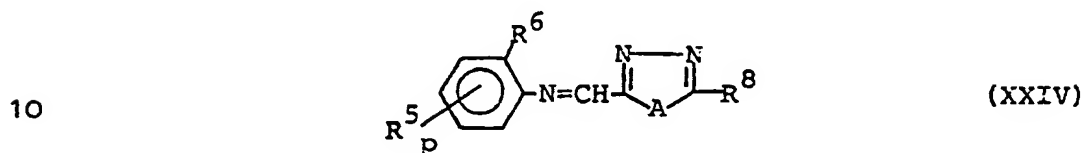
j) the anilines of formula (XII) with azolaldehydes with the formula



in which

5 R^8 has the above-indicated meaning,

is converted in the presence of an inert organic solvent, like toluene, at temperatures between 80 and 120°C, and the resulting compounds with the formula



in which

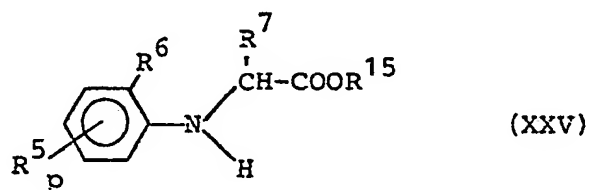
A, R^5 , R^6 , R^8 and p have the above-indicated meaning,

and reduced in a generally known manner; e.g. through mixing with complex hydrides, like sodium borohydride, potentially in the presence of a polar organic solvent like methanol, at temperatures between 0 and 80°C.

The compounds with the formulas (XII) and (XIII) required for process (d) as base materials are known or
20 can be created with known methods (see also Helv. Chim. Acta 55, 199 ff (1972),

Chem.Ber. J32, 797 ff (1899) and Chem.Ber. 9jS, 1049 ff (1963)) .

The base materials for formula (XIV) required for process (e) are not known yet. However, they can be
5 created with known methods by converting known esters (see also DT-OS 2 350 944 and 2 513 730) of the formula



in which

10 R⁵, R⁶, R⁷ and p have the above-indicated meaning, and R¹⁵ stands for methyl or ethyl,

with hydrazinhydrate preferably in the presence of an organic solvent, like ethanol, dioxane or dimethylformamide, at temperatures between

15 20 and 120°C (see also preparation embodiments).

The reaction components of formulas (XV) and (XVIII) required for process (e) are generally known compounds in organic chemistry.

The substances of formulas (XIXa), (XIXb), (XXI) and
20 (XXII) required for process (f) are also known.

The azol-aldehydes of formula (XXIII) required as reaction components for process (j) are also known, or can be created based with known methods (see also Elderfield, "Heterocyclic Compounds", Vol. 1, (1961) and "Advances in
5 Heterocyclic Chemistry, Vol. 9, (1968)).

The halogen-succinic-acid-chlorides or anhydrides required as base materials for the conversion according to process (c) are generally defined in formulas (XIa) and XIb). In these formulas, R⁹ stands preferably for
10 chlorine, bromine and iodine.

The halogen succinic acid chlorides and anhydrides of formulas (XIa) and (XIb) are generally known compounds in organic chemistry.

Dilutants to be used for the conversion (c) are
15 preferably inert organic solvents. They include preferably ketones, like diethylketone, especially acetone and methylethylketone; nitriles like propionitrile, especially acetonitrile; ether, like tetrahydrofuran or dioxane; aliphatic and aromatic
20 hydrocarbons, like petroleum ether, benzene, toluene or xylol; halogenated hydrocarbons, like methylenechloride, tetrachlorocarbon, chloroform or chlorobenzene; and esters like ethyl acetate.

Process (c) can potentially be performed in the presence
25 of acid binders (hydrogen chloride acceptors).

909882/0346

Le A 18 887

As such, any common acid binders can be used. They include preferably organic bases like tertiary amines, e.g. triethylamine or pyridine; also inorganic bases, e.g. alkali-hydroxide and alkali-carbonate.

5

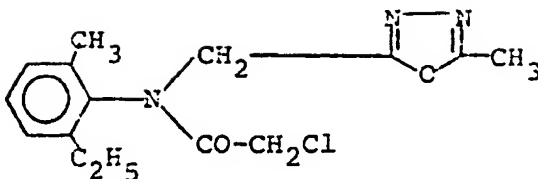
The reaction temperatures for process (c) can be varied over wider range. Generally, the working temperatures are between 0 and 120°C, preferably between 20 and 100°C.

10 In process (c) 1 mol of the compound per formula (X) is preferably matched by 1 to 1.5 mol of a halogen acetylation agent, and by 1 to 1.5 mol of an acid binder. The isolation of the compounds of formula (IV) is performed in the known manner.

The practical preparation of acetanilides of formula (IV) is explained in the following embodiments:

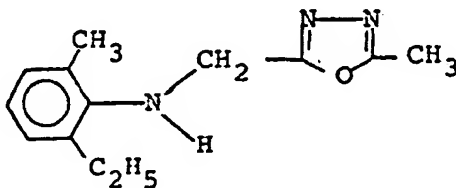
15

Embodiment 88



- 16.3 g (0.07 mol) of 2-ethyl-6-methyl-N-[(2-methyl-1,3,4-oxadiazole-6-yl)-methyl]-aniline and 6 g (0.076 mol) of
- 5 anhydrous pyridine are heated in 100 ml of absolute tetrahydrofuran under agitation to the boiling point, and mixed by drops with a solution of 8 g (0.07 mol) chloroacetylchloride in 20 ml tetrahydrofuran. After all the drops have been added, the mixture is agitated for 10
- 10 minutes, concentrated by distillation of the solvent, and the residue is mixed with 150 ml water. The crystallizing reaction product is suctioned off, washed with water and dried. The result is 18.7 g (87 % of theoretical value) of
- 15 beige-colored crystals of 2-ethyl-6-methyl-N-[2-1,3,4-oxadiazole-5-yl)-methyl]-chloroacetanilide with a melting point 67 to 70°C.

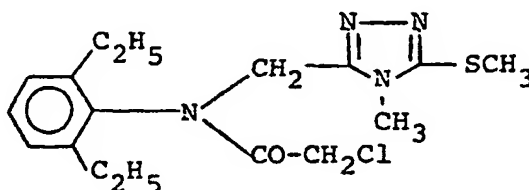
Preparation of the base product



909882/0346

- A mixture of 101.2 g (0.76 mol) of 2-ethyl-6-methyl-aniline, 40 g (0.3 mol) of 5-chloromethyl-1,3,4-oxadiazole, 41.4 g (0.3 mol) powdered potassium carbonate, and 76 ml of diethylformamide is heated for 5
5 hours to 100 °C while constantly agitated. Afterwards, the reaction mixture is filtered, the filtrate is diluted with methylenchloride, and washed several times with water. The methylenchloride phase is dried via sodium sulfate, and concentrated vacuum-distilling the solvent.
10 The residue is vacuum-distilled. The result is 46.8 g (67.5% of the theoretical value) yellowish oil of 2-ethyl-6-methyl-N-[2-methyl-1,3,4-oxadiazole-5-yl)-methyl]-aniline with a boiling point of 140 to 142°C/0.1 mm with a 94% purity (determined with gas chromatograph).

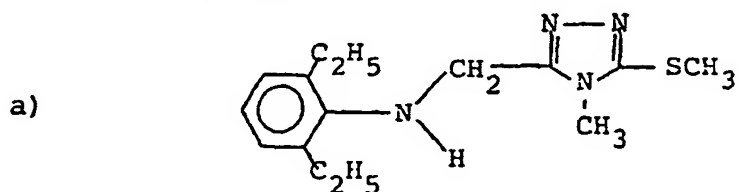
15 Embodiment 89



- 5 g (0.017 mol) of 2,6-diethyl-N-[(1-methyl-2-methylthio-1,3,4-triazole-5-yl)-methyl]-aniline and 1.6 g (0.02
20 mol) pyridine are mixed in 100 ml of absolute tetrahydrofuran, and mixed at room temperature in the form of drops with 2.3 g (0.02 mol) chloroacetylchloride whereby the temperature increases to about 30°C. The mixture is agitated for 2 hours, the mixture is concentrated through distillation of the solvent,

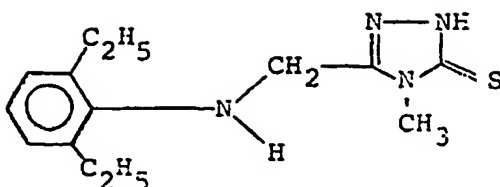
and then mixed with water. The crystallizing product is suctioned off, dried and recrystallized from diisopropyl-ether/ethyl acetate. The result is 5 g (60% of the theoretical value) of 2,6-diethyl-N-[(1-methyl-2-methylthio-1,3,4-triazole-5-yl)-methyl]-chloroacetanilide with a melting point of 121 to 123°C.

Preparation of preliminary stages



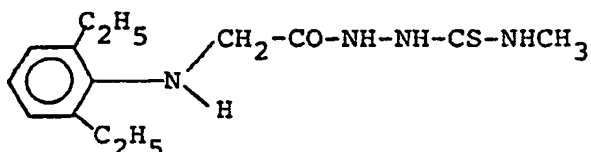
13.9 g (0.05 mol) of 2,6-diethyl-N-[(1-methyl-2-thiono-1,3,4-
10 triazole-5-yl)-methyl]-aniline are mixed at room
temperature in a two-phase mixture of 150 ml toluene and
40 ml 50% sodium hydroxide solution with 1.5 g triethyl-
benzyl-ammoniumchloride (TEBA) as catalyst under fast
agitation with drops of 6.3 g (0.05 mol) dimethylsulfate,
15 whereby the temperature rises to about 35°C. Agitation
continues for 5 hours, the toluene phase is separated,
washed several times with water, dried via sodium sulfate,
and concentrated by distilling the solvent. The residual
oil is crystallized by adding petroleum ether. After
20 recrystallization from petroleum ether, the result is
6.7 g (40 % of theoretical value) of 2,6-diethyl-N-[(1-
methyl-2-methylthio-1,3,4-triazole-5-yl)-methyl]-aniline
with a melting point of 65 to 67 C.

b)



29.6 g (0.1 mol) 1-methyl-4-[(2,6-diethyl-anilino)-acetyl]-thiosemicarbazide are suspended in 150 ml ethanol and - after adding of 7 g potassium hydroxide - heated in 20 ml water for
5 1 hour under reflux. Afterwards, the majority of the solvent is distilled out, and the residue is mixed with 250 ml water. After acidification with pure acetic acid to a pH-value of 5 the resulting precipitate was suctioned off and thoroughly washed with water. After drying, the result is 27 g (97% of
10 the theoretical value) of 2,6-diethyl-N-[(1-methyl-2-thiono-1,3,4-triazole-5-yl)-methyl]-aniline with a melting point of 117 - 121°C.

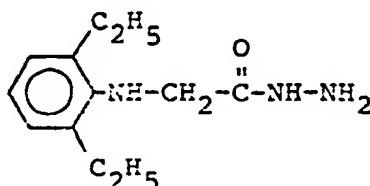
c)



44.2 g (0.2 mol) of 2,6-diethyl-anilino-acetic acid-
15 hydrazide and 14.8 g (0.2 mol) of methyl mustard seed oil are dissolved in 250 ml ethanol, and heated for one hour to reflux temperature. After subsequent cooling to room temperature, the resulting precipitate is suctioned off and washed twice with 50 ml ethanol each. After
20 drying, the result is 46 g (78% of the theoretical value) of 1-methyl-4[2,6-diethyl-anilino)-acetyl]-

-thiosemicarbazide in the form of a colorless crystalline substance with a melting point of 166°C.

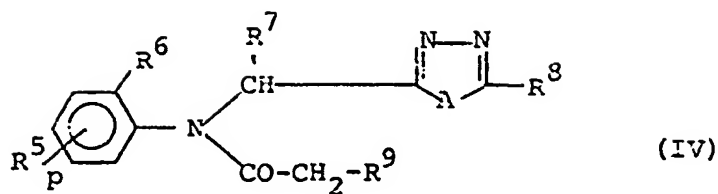
d)


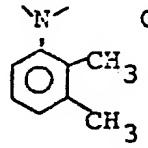


- 5 58.7 g (0.25 mol) of 2,6-diethyl-anilino-acetic acid ethyl-ester and 25 g hydrazinhydrate are kept standing in 200 ml ethanol for 24 hours. Afterwards, the mixture is concentrated by distillation of the solvent, and the residue is stirred out with water.
- 10 After drying, the result is 50.5 g (91% of the theoretical value) colorless crystals of 2,6-diethyl-anilino-acetic-acid-hydrazide with a melting point of 71 to 73°C.

- The compounds listed in Table 5 by formula are obtained
- 15 in the same manner.

Table 5



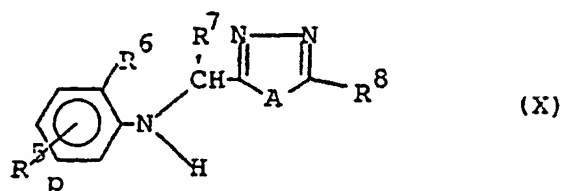
Emb. No.	R ⁷	R ⁸	R ⁶	R ⁵ _P	A	R ⁹	Melting Point °C
90	H	CH ₃	C ₂ H ₅	6-C ₂ H ₅	O	Cl	79-82
91	H	CH ₃	CH ₃	6-CH ₃	O	Cl	91-93
92	H	CH ₃	C(CH ₃) ₃	-	O	Cl	102-104
93	H	-S-CH ₂ -CH=CH ₂	C ₂ H ₅	6-C ₂ H ₅	-N- CH ₃	Cl	67-70°
94	H	-S-CH ₂ - 	CH ₃	6-C ₃ H ₅	-N- CH ₃	Cl	115-20
95	H	C ₂ H ₅	CH ₃	6-C ₂ H ₅	O	Cl	57-59
96	H	C ₂ H ₅	C ₂ H ₅	6-C ₂ H ₅	O	Cl	43-47
97	H	i-C ₃ H ₇	CH ₃	6-C ₂ H ₅	O	Cl	viscous oil
98	H	CH ₃	CH ₃	3-CH ₃		Cl	hardened into a glassy substance
99	H	CH ₃	C ₂ H ₅	6-C ₂ H ₅	O	Br	80°
100	H	CH ₃	CH ₃	6-C ₂ H ₅	O	Br	92-94°
101	H	CH ₃	i-C ₃ H ₇	6-i-C ₃ H ₇	O	Cl	135-37°


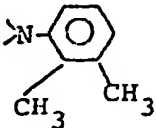
909882/0346

The base products listed in the following table by formula can be obtained with one or more of the processes described in the application.

Table 6

5



Emb. No.	R ⁷	R ⁸	R ⁶	R ⁵ _P	A	Melting Point [°C] and Refractive Index
X-1	H	CH ₃	C ₂ H ₅	6-C ₂ H ₅	O	n _D ²² = 1.540
X-2	H	CH ₃	CH ₃	6-C ₂ H ₅	O	n _D ²² = 1.547
X-3	H	CH ₃	CH ₃	6-CH ₃	O	n _D ²² = 1.552
X-4	H	CH ₃	-(CH ₃) ₃	-	O	52-55
X-5	H	CH ₃	i-C ₃ H ₇	6-i-C ₃ H ₇	O	96-99
X-6	H	C ₂ H ₅	C ₂ H ₅	6-C ₂ H ₅	O	n _D ²² = 1.534
X-7	H	C ₂ H ₅	CH ₃	6-C ₂ H ₅	O	n _D ²¹ = 1.542
X-8	H	i-C ₃ H ₇	CH ₃	6-C ₂ H ₅	O	n _D ²¹ = 1.531
X-9	H	SCH ₃	C ₂ H ₅	6-C ₂ H ₅	>N-CH ₃	65-57
X-10	H	S-CH ₂ -CH=	C ₂ H ₅	6-C ₂ H ₅	>N-CH ₃	n _D ²¹ = 1.577
X-11	H	CH ₂ S-CH ₂ - 	CH ₃	6-C ₂ H ₅	>N-CH ₃	viscous oil
X-12	H	CH ₃	CH ₃	3-CH ₃		142-143

5 The acetanilides of formula (IV) exhibit strong herbicidal, in particular, selective herbicidal properties. They are therefore suitable for selective weed and grass control. The selectivity is not always satisfactory.

10 The antidote to be applied according to the invention - namely N-dichloroacetyl-1.2.3.4-tetrahydro-isochinoline of formula (I) - is especially well suited for the protection of valuable crops like corn, soy beans, cotton, sugar beets, grain, rice, and sugar cane from damages due to herbicides with the use of acetanilides of formulas (II), (III) and (IV) acid addition salts or metal salt complexes of formula (II) agents.

15 The agent combinations according to the invention indicate a very good effect against weeds and grasses on various crops. They can therefore be used for selective weed control in various crops. Weeds - in the broadest sense - are here any plants growing in locations where they are not desired.

20 The agents according to the invention can be used on the following plants, for example:

25 Dicotyle weeds of the genus: Sinapis, Lepidium, Galium, Stellaria, Matricaria, Anthemis, Galinsoga, Chenopodium, Urtica, Senecio, Amaranthus, Portulaca, Xanthium, Convolvulus, Ipomoea, Polygonum, Sesbania, Ambrosia, Cirsium, Carduus, Sonchus, Solanum, Rorippa, Rotala, Lindernia, Lamium, Veronica, Abutilon, Emex, Datura, Viola, Galeopsis, Papaver, Centaurea.

30

Dicotyle crops of the genus: Gossypium, Glycine, Beta, Daucus, Phaseolus, Pisum, Solanum, Linum, Ipomoea, Vicia, Nicotiana, Lycopersicon, Arachis, Brassica, Lactuca, Cucumis, Cuburbita.

- 5 Monocotyle weeds of the genus: Echinochloa, Setaria, Panicum, Digitaria, Phleum, Poa, Festuca, Eleusine, Brachiaria, Lolium, Bromus, Avena, Cyperus, Sorghum, Agropyron, Cynodon, Monochoria, Fimbristylis, Sagittaria, Eleocharis, Scirpus, Paspalum, Ischaemum, Sphenoclea,
10 Dactyloctenium, Agrostis, Alopercurus, Apera.

Monocotyle crops of the genus: Oryza, Zea, Triticum, Hordeum, Avena, Secale, Sorghum, Panicum, Saccharum, Ananas, Asparagus, Allium.

- The agents according to the invention are especially suited
15 for selective weed control in corn, soy beans, cotton, sugar beets, grains, rice, and sugar cane.

- The antidote to be applied according to the invention can potentially be converted into the usual chemical structures like solutions, emulsions, spray powders, suspensions,
20 powders, dusting agents, foams, pastes, soluble powders, granulates, aerosols, suspension-emulsion concentrates, agent-impregnated natural and synthetic materials, micro-encapsulations in polymers, as a mixture together with the herbicides it is supposed to work with.

25

These formulations are manufactured in a known manner,
for example, by potentially mixing the applicable
antidote according to the invention with the herbicidal
agents, for which it is used, including with dilutants,
5 i.e. liquid solvents, pressurized, liquidized gasses,
and/or solid carrier substances, potentially using
surface-active agents, i.e. emulsifiers and/or dispersion
agents or foam-generating agents. If water is used as a
dilutant, organic solutions can also be used as auxiliary
10 solvents. The following liquid solvents can generally be
used: aromatics, like xylol, toluene, alcylnaphthalines,
chlorinated aromatics or chlorinated aliphatic
hydrocarbons like chlorobenzenes, chloroethylene or
methylenechloride, aliphatic hydrocarbons like
15 cyclohexane or paraffins, e.g. petroleum fractions,
alcohols like butanol and glycol as well as ethers and
esters, ketones like acetone, methylethylketone, methyl-
isobutylketone or cyclohexanon, highly polar solvents
like dimethylformamide and dimethylsulfoxide and water;
20 liquidized, gaseous dilutants or carrier substances are
defined as liquids, which are gaseous at normal
temperatures and under normal pressure, e.g. aerosol
propellants like butane, propane, nitrogen, and carbon
dioxide; as solid carrier substances:

25

5 natural stone meals like kaolin (china clay), clays, talcum, chalk, quartz, attapulgit, Montmozillonite or or diatome earth and synthetic stone meals like highly dispersed silicic acid, aluminum oxide and silicates; as solid carrier substances for granulates:

10 broken and fractioned natural rock like calcite, marble, pumice, sepiolithe, dolomite and synthetic granulates of inorganic and organic meals as well as granulates of organic material like saw dust, coconut shells, corn husks, and tobacco stems; as emulsifier and/or foaming agents: non-ionogenic and non-ionic emulsifiers like polyoxyethylene-fatty acid esters, polyoxyethylene-fatty alcohol ether, e.g. alcylyl-arylsulfonate, alcylylsulfate, arylsulfonate as well protein hydrolysate; as dispersion agent: e.g. Lignin-Sulfite bases and methyl cellulose.

15 The formulations may include adhesives like carboxymethyl-cellulose, natural and synthetic powdery, grainy or or latex-type polymers, like Arabism rubber, polyvinyl alcohol, polyvinyl acetate.

20 The use of the following coloring agents is also possible: inorganic pigments, e.g. ferrous oxide, titanium oxide, Ferro-cyan-blue and organic coloring agents like alizarin, ago-metal phthalocyanine coloring agents, and trace nutrients like salts of iron, manganese, boron, copper, cobalt, molybdenum and zinc.

25 The chemical formulations generally contain between 0.1 and 95% weight-percent of the antidote or of the antidote and the herbicide, preferably between 0.5 and 90%.

5 The antidote according the invention can also be used
alone or in its formulations as a mixture with
herbicides agents, whereby pre-formulation or tank
mixtures are available as options. The mixing with
other known agents like fungicides, insecticides,
acarizides, nematizides, agents against bird damage,
growth agents, plant food and soil structure enhancers
is also possible.

10 The antidote or any mixtures of the antidote and
herbicides according to the invention can be used
alone in the form of their formulations or in diluted
formulations like ready-to-use solutions, suspensions,
emulsions, powders, and granulates. Application is in
the known manner, e.g. by pouring, squirting,
15 spraying, dusting or sprinkling.

The antidote to be applied according to the invention
can be applied in compliance with the methods commonly
used for such antidotes. The antidote applicable
according to the invention can be applied before or
20 after the herbicide. An additional option for use is
to apply the antidote into the trench at the time the
seeds are sown.

25

909882/0346

De 2 12 667

Seedlings can be treated with the antidote before they are planted. For the case in hand, areal treatment is preferred.

- 5 The use of the antidote according to the invention is associated with the local quantities of herbicides. These quantities vary between 0.1 and 5 kg/ha. The quantity of the antidote is independent of the herbicide and the quantity of the herbicidal agent.
- 10 Generally, the quantities of the antidote according to the invention for areal treatment are between 0.1 and 5 kg/ha, preferably between 0.2 and 4 kg/ha. In regard to the treatment of seeds, the quantity for antidote according to the invention are generally between 10 and
- 15 300 g per kilogram of seeds, preferably between 25 and 200 g per kilogram of seeds.

- In the agent combinations according to the invention, the antidote-herbicide weight ratios may vary to a relatively large degree. Generally, 1 weight part of
- 20 herbicide agent of formula (II), (III) or (IV) is matched with 0.05 to 1.0 weight parts, preferably 0.1 to 0.5 weight parts, of the antidote of formula (I).

25

The strong effectiveness of the antidote according to

to the invention and/or the combination of agents
according to the invention is shown in the
following embodiment.

Embodiment A

Pre-emergence-Test

Solvent: 5 weight parts acetone

Emulsifier: 1 weight part alcyrarylpolyglycolether

5 In order to produce an effective agent preparation, 1
weight part of the herbicidal agent or the antidote or of
the antidote/herbicide mixture is mixed with the
indicated amount of solvent, the indicated amount of
emulsifier is added, and the concentrate is diluted with
10 water to the desired degree.

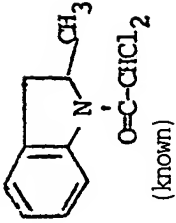
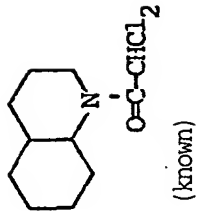
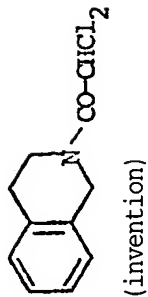
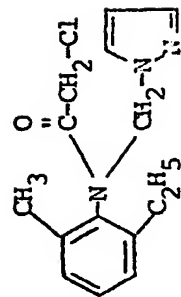
Seeds of the test plants are sown into normal soil, and
after 24 hours doused with the herbicide preparation or
the antidote preparation or with the preparation of
antidote and herbicide. The amount of water per area unit
15 is kept constant. The agent concentration in the
preparation is of no importance; the only important
factor is the quantity per area unit. After three weeks,
the damage on the plants is bonified in % damage in
comparison to the development of untreated control plants
20 with the following meanings:

0 % = no effect (like untreated control)

100 % = total destruction

25 Agents, quantities, and results are listed in the
following table:

Table A
Pre-emergence-Test

Herbicide Agent	Herbicide Agent Quantity kg/ha	Antidote Agent	Antidote Agent Quantity kg/ha	Corn	Echinochloa	Amaranthus
-	-	 (known)	3	0	0	0
-	-	 (known)	3	0	0	0
-	-	 (invention)	3	0	0	0
	3	-	-	90	100	100

67-
62-

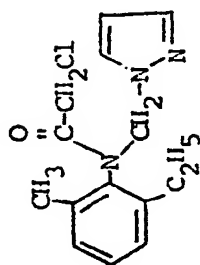
2828222
100

909882/0346

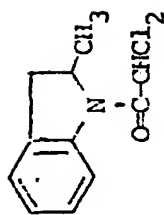
Table A (Continued)

Pre-emergence-Tes

Herbicide Agent	Herbicide Agent Quantity	Antidote Agent	Antidote Agent Quantity kg/ha	Corn	Echinochloa	Amaranthus
-----------------	--------------------------	----------------	-------------------------------	------	-------------	------------



3

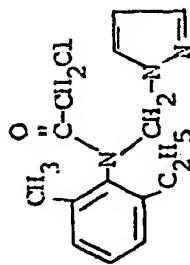


3

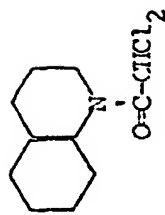
30

100

100



3

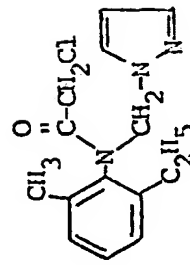


3

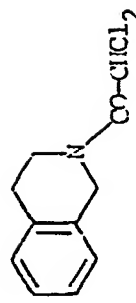
80

100

100



3



3

0

100

100

- 68 -

2828222



EXPERT TRANSLATION BUREAU, INC.

920 W. Lakeside, Suite 2109, Chicago, IL 60640
Telephone: (312) 759-9999 Facsimile: (312) 780-5099
www.Expert-Translation.com

CERTIFICATE OF TRANSLATION

December 5, 2006

I, Angela Christie, hereby certify that I am competent in both English and German languages.

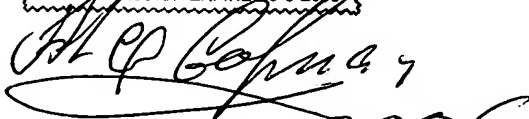
I further certify that under penalty of perjury translation of the aforementioned document:

[DE 2828222 (A1).pdf]

from the German language into the English language is accurate and correct to the best of my knowledge and proficiency.


Professional Translator




12.05.2006